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UV photolysis and mild (60-100°C) thermolysis of aryloxyoxalyl tert-butylperoxides provides a new unimolecular source of aryloxy radicals, as shown by ESR and UV spectroscopy. Some side reactions are noted, but in general the method looks effective as a means of making a fairly stable precursor to phenoxy radicals, with radical generation under straightforward photochemical and thermal conditions. *Journal of Organic Chemistry*, Preprints.

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CONVENIENT UNIMOLECULAR SOURCES OF ARYLOXYL RADICALS.
II -- ARYLOXYOXALYL tert-BUTYLPEROXIDES

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CONVENIENT UNIMOLECULAR SOURCES OF ARYLOXYL RADICALS. II – ARYLOXYOXALYL *tert*-BUTYLPEROXIDES

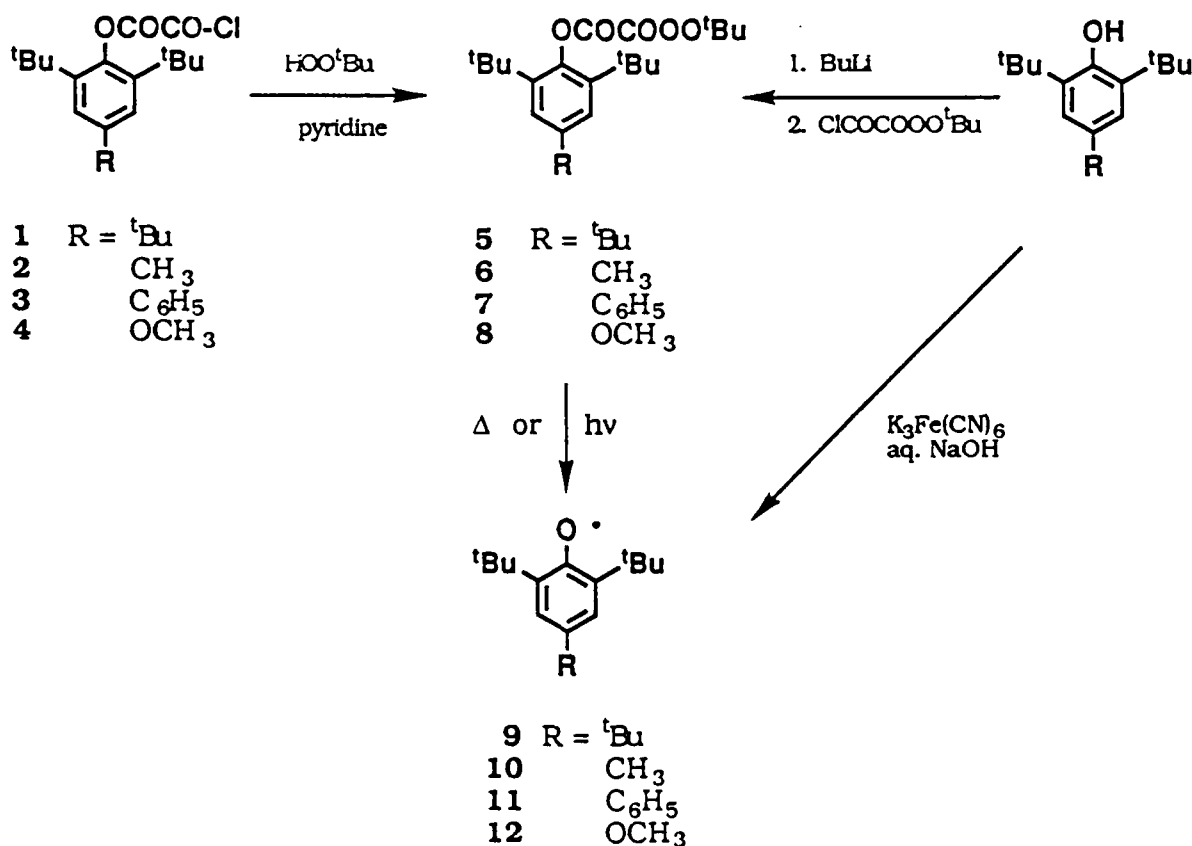
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Abstract: UV photolysis and mild thermolysis of aryloxyoxalyl *tert*-butylperoxides provides a new unimolecular source of aryloxy radicals, as shown by ESR and UV-vis spectroscopy.

As noted in the preceding paper,^{1a} unimolecular methods for generating aryloxy radicals^{1b} – especially under rigid matrix conditions -- appear generally to have been lacking, save for direct O-H photolysis in precursor phenols.² Hence, efficient means to carry out aryloxy generation in matrix would be a useful addition to the pantheon of methods for producing and studying radicals and polyradicals of related nature. In this communication we report the synthesis of some aryloxyoxalyl *tert*-butylperoxides and show their use as convenient, effective unimolecular photochemical and thermal aryloxy precursors.

In one synthetic procedure, aryloxyoxalyl chlorides (AOC's) 1-4 were synthesized as in the preceding paper.¹ The appropriate AOC was then dissolved in diethyl ether and treated with one equivalent of *tert*-butyl-



hydroperoxide dissolved in ether/pyridine at 0°C, stirred for 30 min, extracted sequentially with 10% H₂SO_{4(aq)}, 10% NaHCO_{3(aq)}, and water, then the organic residue dried over MgSO₄ and evaporated to give the desired aryloxy *tert*-butylperoxide (AOB), which may be recrystallized in pentane at low temperatures. AOB's 5-7³ were readily synthesized by this method, and appear to be indefinitely stable at -20°C under nitrogen.

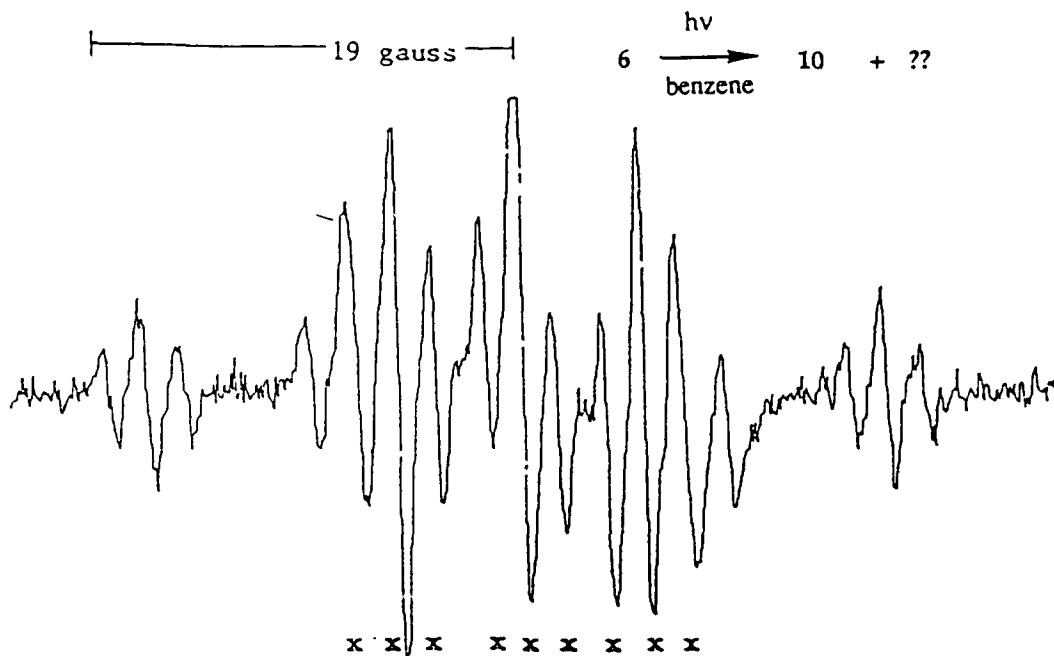
Attempts to make AOB 8 by this method failed. By an alternative procedure, efforts to add *tert*-butylperoxyoxalyl chloride (DANGER: EXPLOSION HAZARD⁴) to the lithium salt of 2,6-di-*tert*-butyl-4-methoxyphenol in benzene or pentane at 0°C gave instant production of a deep red solution with UV-vis identical to that of the stable radical generated by oxidation of the phenol. ESR spectroscopy confirms that radical 12 is produced under these conditions, presumably through intermediacy of a highly unstable AOB 8.

Irradiation of the stabler AOB's 5-7 (degassed benzene, unfiltered 1000 W Xenon arc) in solution quickly yielded the characteristic colors and UV-vis spectra of radicals 9-11, with ESR spectra similar to those noted by solution oxidation of the corresponding phenols⁵ and by photolysis of AOC's 1-3.¹ The spectrum from photolysis of 6 also shows a radical impurity (arrows, Figure 1, following page). The other spectra show no obvious similar impurities. We tentatively identify the unknown portion of the ESR in Figure 1 as a benzylic radical derived from abstraction of the active methyl group in 6 by *tert*-butoxyl radical generated in the photolysis. Thermolysis of AOB's 5-7 (degassed benzene, 75°C, 15-60 min) yields bubbles, and is accompanied by the typical color changes indicating stable radical formation, with production of persistent ESR spectra confirming presence of 9-11.

The lifetimes of radicals 9-11 appears substantially longer than those of the corresponding AOB's at elevated temperature. Whereas solutions of 9-11 require overnight heating in benzene under nitrogen to discharge their color, observation of thermolysis of the AOB ester of phenol in CCl₄ at -60°C shows complete depletion of the starting *tert*-butyl peak at δ 1.38 ppm, and concurrent appearance of decomposition product peak⁶ at δ 1.18 ppm (Figure 2, following page). The half-life of decomposition is approximately 90 min under these conditions. A more precise study of kinetics as a function of substituent R in the AOB's is in progress.

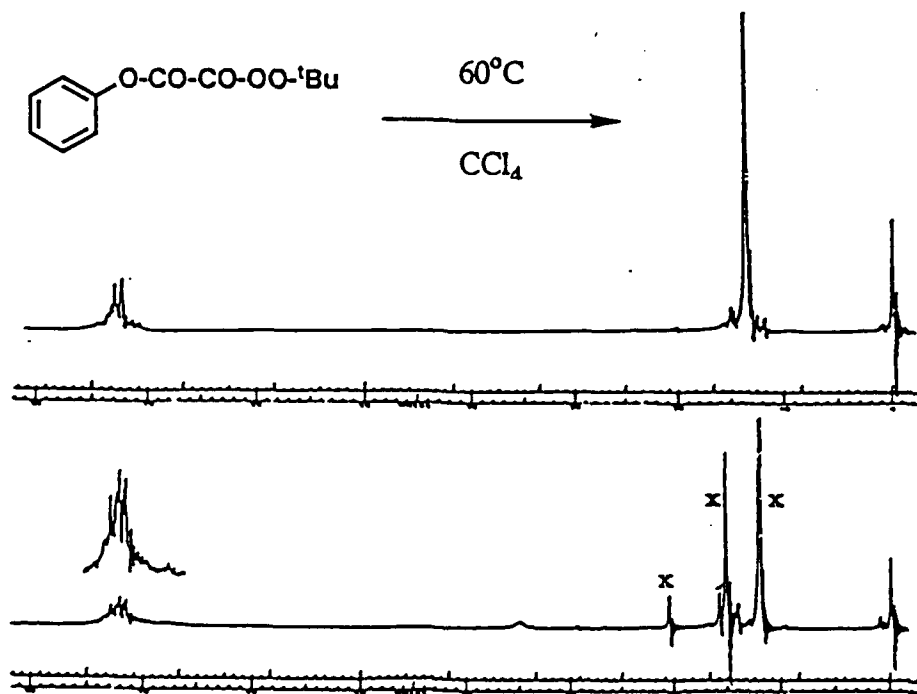
The utility of the AOB's is somewhat different from that of the AOC's described in the preceding paper. The stability of AOC's¹ seems somewhat greater than that of AOB's, as shown by our failure to isolate AOB 8. However, where the AOB's are stable they seem to be of near-equal photochemical utility as aryloxy precursors. In addition, AOB's readily produce aryloxy radicals under very mild thermolytic conditions. We are particularly interested in the possibility that AOB's and related molecules may serve as aryloxy precursors at elevated temperatures in inert polymer matrices. These results and those of the preceding paper present two convenient, efficient unimolecular means for photochemical and thermal production of aryloxy radicals in solution and in some rigid matrix conditions. Other

Figure 1: ESR spectrum Obtained from Photolysis of AOB ester 6.



The ESR spectrum was obtained in degassed benzene solution at room temperature at 9.79 GHz, after irradiation for 5-20 min with a 1000W Xenon arc lamp (Kratos). The spectral width scale is indicated in the spectrum in gauss. The suspected benzylic impurity peaks are indicated by x's – other peaks are attributable to phenoxyl radical 10 by comparison to other spectra of 10.

Figure 2: ^1H NMR Spectra Following Thermal Decomposition of the AOB Ester of Phenol at 60°C.



Both ^1H NMR spectra were obtained at 60°C in carbon tetrachloride at 60 MHz. The upper trace shows the zero-time spectrum before significant reaction occurs, the lower trace shows the spectrum at a time of 19 h. X's in the lower trace indicate the final peaks of the decomposition products. The rightmost peak in the spectra is tetramethylsilane.

variations on the general theme of this work may readily be imagined. Further investigation of these possibilities and upon the decomposition mechanisms is in progress, and will be reported in due course.

Acknowledgements: This work was supported by the Office of Naval Research. ESR spectra were obtained at the Department of Polymer Science and Engineering at the University of Massachusetts at Amherst, on an IBM Instruments ESP-9 ESR spectrometer that was purchased with the aid of a grant from the International Business Machines Corporation. A portion of the work described herein was presented at the 197th American Chemical Society Meeting at Dallas, Texas on April 12, 1989.

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1. (a) D. A. Modarelli, F. C. Rossitto, P. M. Lahti, *Tet. Lett.*, preceding paper in this issue. (b) Alkoxy radical generation methods are better known, *e.g.*, in the study of di-*tert*-butylperoxyoxylate by P. D. Bartlett, E. P. Benzing, R. E. Pincock *J. Am. Chem. Soc.*, 82, 1769(1960)
2. A. R. Forrester, J. M. Hay, R. M. Thomson, Chapter 7 of *Organic Chemistry of Stable Free Radicals*; Academic Press, New York, NY, 1968.
3. These new compounds were characterized by spectral methods. Their instability prevented acceptably reproducible elemental analyses or safe distillation of 6. The *tert*-butyl region of the ^1H NMR (δ 1.1-1.4 ppm) was particularly useful for evaluating purity of the samples.

5 – mp 104-105°C. IR(CHCl_3 , cm^{-1} , C=O str): 1760, 1780.
 ^1H NMR(CDCl_3 , 80MHz): δ 1.35(s,18), 1.42(s,9), 1.46(s,9), 7.34(s,2)

6 – (yellow oil) IR(CHCl_3 , cm^{-1} , C=O str): 1760, 1795.
 ^1H NMR(CDCl_3 , 80MHz): δ 1.21(s,18), 1.41(s,9), 2.28(s,3), 6.96(s,2)

7 – mp 103-104°C. IR(CCl_4 , cm^{-1} , C=O str): 1760, 1790.
 ^1H NMR(CDCl_3 , 80MHz): δ 1.40(s,18), 1.42(s,9), 7.2-7.7(m,7)
4. This compound was synthesized by reaction of excess oxalyl chloride with *tert*-butylhydroperoxide at reduced temperature. We recommend that it be made in amounts smaller than 2 g and stored under nitrogen at -20°C for short times only – preferably it should be used upon synthesis. On one occasion a 5 g sample decomposed with considerable vigor upon being allowed to stand for an extended period at room temperature.
5. E. Muller *et al.*, *Just. Liebigs. Ann. der Chem.*, 645, 1, 25, 53, 79(1961).
6. Although decompositions in various solvents give different product *tert*-butyl peaks, all give peaks at substantially different chemical shifts from the starting AOB esters. We have not yet made any effort to characterize the *tert*-butyloxy derived products from this reaction, but intend to report further on these products when complete kinetic and product analysis studies have been completed.